III.B.4 Hexaaluminate Reforming Catalysts

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Objectives

- Develop a durable, low-cost middle distillate reforming catalyst with improved thermal stability and greater resistance toward carbon formation.
- Evaluate activity and selectivity of transition metal doped hexaaluminate catalysts.
  - Correlate activity and selectivity at various levels of transition metal doping.
  - Evaluate the thermal stability and reductive resistance of hexaaluminate catalyst systems.
  - Evaluate carbon formation characteristics.

Approach

- Synthesize and characterize transition metal doped hexaaluminate catalysts.
- Evaluate catalyst activity by turnover frequency (TOF) with model fuel compounds.
- Examine the effect of transition metal doping level on activity and selectivity.
- Examine carbon formation characteristics by post experiment analysis.
- Evaluate long-term stability.

Accomplishments

- Set up new test facilities for continuous unattended operation (operation up to 982°C and 80 psig).
- Synthesized $LaCoAl_{11}O_{19}$, $LaFeAl_{11}O_{19.5}$, $LaNiAl_{11}O_{19}$ catalyst samples.
- Identified optimal processing conditions for active phase formation and maximum surface area.
- Performed reductive stability experiments on $LaCoAl_{11}O_{19}$, $LaFeAl_{11}O_{19.5}$, and $LaNiAl_{11}O_{19}$ using temperature-programmed reduction (TPR) in 5 vol% H_2/Ar.
- Performed partial oxidation activity and selectivity screening experiments on the $LaNiAl_{11}O_{19}$ catalyst with CH_4; O/C = 1.0 at 850°C and 2 atm.
- Demonstrated 165 hours of operation on $LaNiAl_{11}O_{19}$ catalyst with CH_4 partial oxidation; O/C = 1.0 at 850°C and 2 atm.

Future Directions

- Improved catalyst durability:
  - Optimize active metal dopant level.
- Improved catalyst activity:
  - Evaluate activity and selectivity of platinum group metal doped hexaaluminate catalysts.
- Improved carbon formation resistance:
  - Evaluate the effect of alkaline earth doping on carbon formation.

- Improved sulfur resistance:
  - Evaluate the effects of high-temperature operation on sulfur resistance.
- Evaluate bi-metallic dopant combinations for sulfur resistance.

Introduction

The most promising route to hydrogen production from middle distillate fuels is catalytic reforming. For this application, the National Energy Technology Laboratory (NETL) is developing a new class of catalysts based on hexaalumina. Hexaalumina is of interest primarily due to its layered spinel structure that has been shown to be stable at high temperatures (1, 2). Catalytically active metals are doped directly into the structure, resulting in a highly dispersed catalyst system that has been shown to possess reductive stability (3, 4). This project is in its early stages with new test facilities having been constructed and initial catalyst synthesis and characterization having been undertaken.

Approach

A series of catalysts based on transition metal doped hexaalumina, with the general formula $AB_yAl_{12-y}O_{19-z}$, were prepared by co-precipitation from nitrate salt precursors. Catalyst activity, selectivity and reductive resistance will be investigated as a function of A-site (A = La, Ca, Sr and Ba) and B-site (B = Co, Fe, Ni, Rh, Pt, Pd) dopant type and concentration.

Methane partial oxidation will be used to initially screen catalysts for activity and selectivity. N-tetradecane and 1-methyl naphthalene will be utilized as model diesel fuel compounds. Catalyst activity will be measured fundamentally by TOF. Conversion activity, selectivity and carbon formation characteristics will be investigated at various temperatures, O/C ratios and space velocities. Catalyst reductive resistance will be assessed by TPR.

Characterization of hexaalumina catalysts will include active surface area determination, average crystallite size, active phase and surface composition. Post reaction analysis will consist of temperature-programmed oxidation (TPO) and scanning electron microscopy (SEM) for carbon forms and active surface area.

Figure 1. Catalyst Test Facility

Results

Figure 1 shows the new test facility that was constructed and instrumented for continuous and unattended operation. The facility consists of two isothermal fixed-bed reactors capable of operation at 982°C and 80 psig. Online gas phase analysis is determined by gas chromatograph-flame ionization detector (GC-FID) and mass spectrometer. The units are capable of simultaneous water and liquid hydrocarbon feeds. TPR and TPO of catalyst samples can be performed in-situ.

The reduction resistance of $LaCoAl_{11}O_{19}$, $LaFeAl_{11}O_{19.5}$, $LaNiAl_{11}O_{19}$ catalysts was determined by TPR in 5 vol% H_2/Ar. Figure 2 is a plot comparing the TPR spectra for these catalyst samples. $LaCoAl_{11}O_{19}$ showed a single reduction peak at 1093°C, indicating the reduction of Co^{+2} to Co^0. $LaFeAl_{11}O_{19.5}$ showed two reduction peaks; the first, located at 407°C, is the reduction of Fe^{3+} to Fe^{2+}. The second peak, located at 1098°C, is the reduction of Fe^{2+} to Fe^0. $LaNiAl_{11}O_{19}$ exhibited a single broad reduction peak at 1017°C, indicating the reduction of Ni^{2+} to Ni^0. All samples exhibited a high degree of reduction stability.

Figure 3 shows the conversion activity and selectivity for CH_4 partial oxidation over

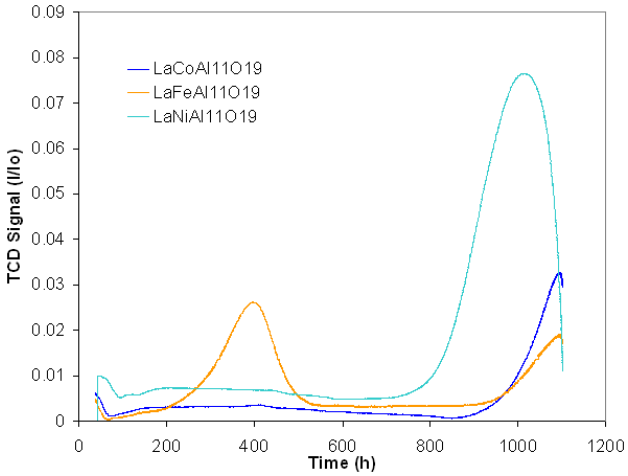

Figure 2. TPR of $LaCoAl_{11}O_{19}$, $LaFeAl_{11}O_{19.5}$, $LaNiAl_{11}O_{19}$ Catalysts in 5 vol% H_2/Ar

$LaNiAl_{11}O_{19}$, conducted at O/C = 1.0, T = 850°C, P = 2 atm and gas hourly space velocity = 16,713 $cm^3h^{-1}g^{-1}$. The catalyst was first pre-reduced in 5 vol% H_2 at 900°C for 1 hour. The selectivity toward H_2 and CO (H_2/CO = 2.0-2.1) was stable over 165 hours of operation. An average CH_4 conversion of 87% was obtained..

Conclusions

Hexaaluminate catalysts exhibited a high degree of reductive stability as determined by TPR. CH_4 partial oxidation experiments on $LaNiAl_{11}O_{19}$ indicate that this catalyst is very active for partial oxidation and exhibits a high selectivity toward H_2 and CO.

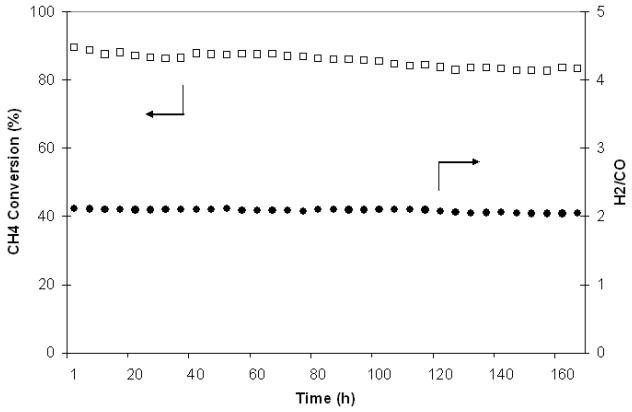

Figure 3. CH_4 Conversion and Selectivity of $LaNiAl_{11}O_{19}$

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FY 2004 Publications/Presentations

1. Chemical Engineering Seminar, presentation to West Virginia University in April

2. SECA Core Conference Review

3. Partial Oxidation of n-Tetradecane over LaNi-Hexaaluminate, accepted to AIChE conference in November